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Sept 13, 1991

Final Report for ONR grant N 00014-84-C-0619

Dear Mr. Biddle,

Enclosed is a copy of information sent to my program manager, Dr. Edward Green of ONR Ocean Chemistry. Essentially this comprises our final report. Our research is ongoing with renewed funding under ONR grant N00014-90-J-4129. If you need additional information please let me know.

Sincerely,

John H. Martin
Director

Iron and DOC Studies in the World Ocean (ONR N 00014-84-C-0619)

by John H. Martin
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ABSTRACT

There is a great deal of concern about the ever-increasing concentration of carbon dioxide in the atmosphere and it is generally acknowledged that the resulting greenhouse effect will cause higher global temperatures and changes in the earth's climate. During the last 100 years, expanding industrialization and fossil fuel burning have brought the CO2 level to ~ 355 ppm, a value subtantially higher than any observed in recent geological history. Analyses of ancient air trapped in Antarctic ice indicate that CO2 amounts have varied over the last 160,000 years from a low of ~ 200 ppm during the ice ages (glacials) to a high of ~280 ppm during the warm periods between the ice ages (interglacials). If we could better understand the reasons for these natural variations in atmospheric CO2 concentrations, we would be in a better position to forecast changes brought about by man's perturbation of the environment.

Although the factors responsible for the glacial/interglacial changes in CO2 levels are not understood, it is thought that oceanic processes are responsible since the ocean contains an equivalent of 60 times as much CO2 as that in the atmosphere. Many also believe that changes in the functioning of the ocean "biological pump" --phytoplankton growth in surface waters with photosynthetic uptake of CO2 and sinking away of carbon-rich plant remains from the surface to deep ocean -- played a dominant role in bringing about the changes in glacial/interglacial atmospheric CO2 levels. Our research is directly related to this problem in two ways:

1. Dissolved organic carbon measurements. In order to understand the functioning of the biological pump and the oceanic carbon cycle in general, it is necessary to understand how carbon cycles through various particulate and dissolved reservoirs. Until recently, most emphasis has been on particulate carbon; however, last year Drs. Sugimura and Suzuki described a new high-temperature catalytic oxidation method for the measurement of dissolved organic carbon (DOC) in seawater. Their results indicate that the DOC pool is much larger than previously believed and that, furthermore, a strong negative relationship exists between DOC and apparent oxygen utilization (AOU). The DOC/AOU relationship suggests that the consumption of DOC, not particulate organic carbon, may be responsible for the utilization of oxygen in the deep ocean. Obviously, it is very important to seek independent confirmation of these results since these findings may entirely change our understanding of how the ocean functions. We have been working in cooperation with Dr. Suzuki and other interested scientists (e.g., Brewer, WHOI; Williams, Scripps) in the devlopment of this technology and should achieve full analytical capability in

1989. Samples for OC analyses will be colle ed during Antarctic and northeast Atlantic cruises during the first half of 1989.

2. Iron as a limiting nutrient. We are also testing the hypothesis that one of the most important factors controlling the functioning of the above-mentioned biological pump is the open ocean availability of the essential plant nutrient, iron. Because of its insolubility in seawater, iron required for the phytoplankton's synthesis of chlorophyll must come from the fallout of iron-rich atmospheric dust. And, in some cases, present-day atmospheric Fe input rates are so low that major plant nutrients such as PO_4 and NO_3 remain unused in well-lit surface waters; i.e., we suspect that Fe deficiency is responsible for the excess major nutrients occurring in the northeast Pacific subarctic, the equatorial Pacific, the Southern (Antarctic) Ocean, and in the northeast Atlantic. The nonuse of these major nutrients indicates that the present-day biological pump is functioning at much less than its full capacity. In contrast, during the last glacial maximum when the pump was believed to be working at full strength, global Fe availability was much enhanced because wind speeds were 1.5 times higher, tropical arid areas 5 times larger, and as a result of these strong winds and aridity, iron-rich atmopsheric dust loads were 10-20 times higher.

Thus far we have measured iron distributions and performed iron enrichment experiments in the northeast Pacific, the northeast Atlantic, the Southern Ocean and equatorial Pacific. Evidence of iron deficiency supporting our hypothesis was found in all of these diverse environments. We have also suggested that Fe fertilization might represent a means to stimulate the active removal of greenhouse gas CO_2 from the atmosphere. This idea has been evaluated in NAS NRC workshops and will be again considered in an ASLO symposium in February 1991. Hopefully it will lead to the planning and implementation of a large scale Fe enrichment experiment to be undertaken in the 1990s.

Long term GOALS:

1. Perfect the methodology necessary for the accurate measuremnt of DOC and DON in sea water using the new high temperature catalytic oxidation technique of Sugimura and Suzuki.

2. With the accomplishment of goal 1, determine the relative importance of atmospheric, continental margin, and in situ biogenic DOC/DON input processes.

3. Determine whether glacial/interglacial ocean iron availability has a direct effect on ocean productivity which in turn leads to an inverse relationship to atmospheric carbon dioxide concentrations.

4. Determine if it feasible to fertilize major-nutrient rich ocean areas with iron in order to stimulate the active removal of CO2 from the atmosphere.

Near Term OBJECTIVES:

1. Finish analyses of samples collected during the 1989/90 Southern Ocean, the 1989 northeast Atlantic Bloom and 1990 equatorial Pacific cruises.

APPROACH:

1. Our approach is to measure dissolved and particulate iron distributions in various ocean waters in order to demonstrate that ocean water is basically infertile unless iron is supplied via continental weathering (nearshore) or atmospheric (offshore) processes.

2. In waters that have excess major nutrients, perform enrichment experiments that show that the addition of nannomolar amounts of iron will result in phytoplankton growth, but not in controls without added iron.

3. If DOC is as important as recent findings suggest, it is important to measure concentrations in high latitude regions where waters are sinking away from the surface; i.e., the Southern Ocean and the North Atlantic.

TASKS COMPLETED:

1. Samples were collected and experiments were performed sucessfully during the 1989 North Atlantic spring bloom study, the 1990 Ross Sea cruise and the 1990 equatorial Pacific cruise.

RESULTS:

1. We obtained direct evidence that iron enrichment stimulated the uptake of CO2 during the North Atlantic bloom study. We also found evidence of Fe deficiency in waters south of Iceland (59.5N). Aliquots of water samples were collected from Dr. Suzuki for future DOC/DON analyses and comparisons.

2. Evidence that Fe deficiency is limiting phytoplankton growth in the Southern Ocean was found during the January/February, 1990 Ross Sea cruise. It was also determined that atmospheric dust leachate Fe stimulated phytoplankton growth during the June/July, 1990 cruise to the equatorial Pacific.

3. We have obtained DOC concentrations similar to those measured by Dr. Suzuki on replicate samples collected during the north Atlantic bloom cruise.

ACCOMPLISHMENTS:

1. Developed the hypothesis that global iron availability and its effect on ocean phytoplankton productivity may be directly related to glacial/interglacial changes in atmospheric CO2 abundance.

2. With the perfection of ultraclean techniques, we were among the first to show that open Pacific iron concentrations were so low that it was not possible for phytoplankton to grow without the addition of supplemental iron from atmospheric input processes.

3. Although there are countless historical examples for the terrestrial environment, we were the first to demonstrate that the lack of a trace element (iron) limits plant growth in the marine environment.

4. There is enough interest in the potential for ocean Fe fertilization as a means of actively stimulating CO2 removal from the atmopshere to warrent presentation at 3 meetings called for and/or sponsored by the NRC. Iron research will also be discussed at an ASLO symposium to be held in February 1991.

------------------------Publications---------------------------------

P-88 Martin, J.H. and S. Fitzwater. Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic. Nature, 331: 341-343 (1988).

P-88 Martin, J.H. and R.M. Gordon. Northeast Pacific iron distributions in relation to phytoplankton productivity. Deep-Sea Res. 35: 177-196 (1988).

P-89 Martin, J.H., R.M. Gordon, S. Fitzwater, and W.W. Broenkow VERTEX: phytoplankton/iron studies in the Gulf of Alaska. Deep-Sea Res. 36: 649-680 (1989).

P-89 Yarbrough, M.A., W.W. Broenkow, R.E. Reaves. An integral CTD rosette optical profiler. Mar. Tech. Soc. J. 23 (1989)

R-89 Breaker, L.C. and W.W. Broenkow. The circulation of Monterey Bay and related processes. MLML Tech Rep. 1989-1

P-90 Martin, J.H. Glacial-Intergalacial CO2 Change: the Iron Hypothesis. Paleoceanogr. 5: 1-13 (1990).

P-90 Martin, J.H., R.M. Gordon and S. Fitzwater. Iron in Antarctic Waters. Nature 345: 156-158 (1990).

P-90 Martin, J.H., W.W. Broenkow, S.E. Fitzwater and R.M. Gordon. Yes it does: A reply to the comment by Banse. Limnol. Oceanogr., 35: 775-777 (1990).

P-90 Martin, J.H., S.E. Fitzwater and R.M. Gordon. Iron deficiency limits phytoplankton growth in Antarctic waters. Global Biogeochem. Cycles 4: 5-12.

PS-91 Martin, J.H., S.E. Fitzwater, R.M. Gordon, N.W. Tindale, M.W. Peacock and R.A. Duce. Atmospheric iron stimulates phytoplankton growth in the equatorial Pacific. (in revision).

PI-91 Martin, J.H. Iron, Liebig's Law and the Greenhouse. Oceanography (in press).

PI-91 Martin, J.H., S.E. Fitzwater and R.M. Gordon. We still say iron deficiency limits phytoplankton growth in the subarctic Pacific (J. Geophys. Res. Oceans, in press as a reply to Karl Banse).

------------------------Invited talks, seminars etc.--------------------

IC-88 GOFS: The North Atlantic Plan. AGU, New Orleans Jan 18, 1988

IC-88 Iron Abundance in relation to phytoplankton productivity and growth. AGU New Orleans, Jan 21, 1988

IC-88 Ocean Iron, keystone element or just another trace metal? WHOI Journal Club Lecture July 18, 1988

IC-88 Recent DOC/Iron studies. Global Change Institute, Snow Mass Colorado, Aug 7-21, 1988.

IC-88 Iron as a limiting nutrient in high NO3 environments, ONR ML-ML meeting Santa Barbara, CA, Nov 2, 1988

IC-88 Ocean Iron distribution in relation to phytoplankton productivity. AGU San Francisco, Dec 9, 1988

IC-89 Iron in relation to phytoplankton productivity. Scripps Ecology Group, Feb 15, 1989
Ecology Group, La Jolla, CA, Feb 15, 1989.

IC-89 Iron as a limiting nutrient in the Gulf of Alaska. Univ. of Washington, March 22, 1989.

IC-89 Prospects for control of oceanic carbon cycle; presented as part of: The Contemporary Perturbed Carbon Cycle, NAS, Washington, D.C. March 29, 1989

IC-89 Oceanic Iron Studies, University of Hawaii, July 21, 1989

IC-89 The Iron Story. Gordon Conference on Chemical Oceanography KUA, Meriden, New Hampshire, Aug 18, 1989.

IC-89 A little Geritol Fix for the Greenhouse? SJSU, Soc. of Archimedes Fall Dinner Speech, Oct 13, 1989.

IC-89 The Iron Story, Hopkins Marine Station, Pacific Grove, CA Nov 16, 1989

IC-89 Limits to New Primary Production (in the Southern Ocean): The Iron Hypothesis, NAS meeting: Reducing Global Warming by Enhancing CO2 assimilation in phytoplankton. Washington, D.C. Dec 4, 1989

IC-89 Studies on Oceanic Iron as a limiting factor, PACCHEM 89 The 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, Dec 18, 1989

IC-90 The Iron Story and a Novel Approach to Reverse Global Warming. Workshop on the potential of molecular biological tools for addressing global ocean problems. Ocean Studies Board NRC, Monterey, Feb 3, 1990.

IC-90 Phytoplankton/Iron Studies During the JGOFS Spring Bloom Study AGU/ASLO New Orleans Feb 12, 1990.

IC-90 Iron Studies in the southern ocean. Biogeochemistry of the southern ocean, July 5, 1990 Brest, France.

IC-90 Iron Studies, July 16, 1990 IAEA Laboratory, Monaco

IC-90 Iron studies in the Antarctic and Equatorial Pacific. Sept 18, 1990 Graduate School of Oceanography URI, Narragansett.

IC-90 Iron research in the southern ocean. JGOFS southern Ocean workshop LDGO, Oct. 2, 1990.

IC-90 Microalgae and the iron hypothesis; presented at NRC marine algal productivity and carbon dioxide assimilation workshop; UC Irvine. Oct. 29, 1990.

IC-90 Iron, ice ages and the greenhouse. Point Lobos Docents, Carmel CA. Nov. 3, 1990.